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Boron doping effects on microcrystalline silicon film roughness studied by spectroscopic ellipsometry

Xinli Li [a, b], Lihua Li [a], Zhanhong Ma [a], Jingxiao Lu [b], Alex A. Volinsky [c], Fengzhang Ren [a, *]

[a] Materials Science & Engineering School, Henan University of Science & Technology, Luoyang 471023, China
[b] The Key Laboratory of Materials Physics of Ministry of Education, School of Physics and Engineering, Zhengzhou University, Zhengzhou 450052, China
[c] Department of Mechanical Engineering, University of South Florida, Tampa, FL 33620, USA

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ABSTRACT

Microcrystalline silicon thin films were prepared in the p-type chamber using radio frequency plasma enhanced chemical vapor deposition. The surface roughness evolution of microcrystalline silicon thin films was investigated with spectroscopic ellipsometry (SE). The differences between the real-time SE and *ex-situ* SE have been studied. The effects of boron doping on the surface roughness have been analyzed using real-time SE. For the intrinsic microcrystalline silicon thin films, with an increase in the deposition time, the surface roughness exhibited the following behavior: (a) quickly increased, (b) gradually increased, (c) slightly increased. In the case of boron-doped microcrystalline silicon thin films, the surface roughness showed different behavior: (a) slightly increased, (b) quickly increased, (c) rapidly dropped, (d) increased again. Based on the KPZ model, the intrinsic silicon thin film growth exponent β is about 0.4, corresponding to limited diffusion model. In contrast, boron-doped silicon thin films behavior cannot be described by the KPZ model. Boron catalysis effects promote the reaction radical BH_x aggregation, and result in shadowing. Boron doping changed the film growth process.

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1. Introduction

Recently, hydrogenated micro/nanocrystalline silicon films has been a subject of scientific and technological interest due to their potential applications in optoelectronic devices, such as single electron transistors, solar cells and thin film transistors [1]. These films possess many desirable properties, such as high conductivity, high transport factor, low activation energy, good photo thermal stability, high photo-absorption coefficient, and are easy to dope [2–4]. Boron-doped microcrystalline silicon (μc-Si:H) thin films are used for the window layer of p-i-n junction solar cells due to their high conductivity and high transparency [5–7]. The quality of boron-doped μc-Si:H film plays a key role in the performance of solar cells, due to the window layer, doping layer and the seed of the intrinsic absorbing layer. High quality boron-doped μc-Si:H films have high crystalline volume fraction, thin amorphous incubation layer, high surface roughness, and so on. Its optical and structural properties have been widely studied. Recently, Sucheta Juneja et al. [1] systematically studied the influence of diborane (B_2H_6) doping on the microstructural and optoelectronic properties of p-type nc-Si:H thin films. Ke Tao [8] and Teng Ge [9] studied the influence of substrate temperature on the p-μc-Si:H and intrinsic μc-Si:H structure and properties, respectively. Jinjoo Park et al. [10] studied the effects of thermal annealing on optical and electrical properties of boron doped a-SiO_x:H thin films. The surface roughness of μc-Si:H film strongly correlates with the growth mechanism. For the μc-Si:H films, the process parameters, such as the substrate temperature, silane concentration and boron doping concentration have important effects on the surface roughness.

Surface roughness can be characterized with atomic force microscopy (AFM) and spectroscopic ellipsometry (SE). There are also many *ex-situ* measuremental techniques, including X-ray diffraction, AFM, and Raman spectroscopy to investigate the μc-Si:H grain growth process. SE possesses fast, non-destructive and precise optical characteristics. SE mainly analyzes the change of incident light and reflected light polarization state. Spectroscopic techniques have been widely used in measuring film thickness and optical parameters [11–14]. It is an effective method to characterize optical and structural properties of amorphous silicon (a-Si:H) films and μc-Si:H films. Kumar et al. [15] studied a-Si:H and μc-Si:H films obtained by glow discharge deposition using SE. Gu et al. [16,17]

* Corresponding author.
E-mail address: lyrenfz@163.com (F. Ren).

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analyzed the growth of the μc-Si:H films deposited with very high frequency plasma-enhanced chemical vapor deposition (VHF-PECVD) method using *ex-situ* SE. Joohyun Kohd et al. [18] studied the effect of different boron dopant source gases on the nucleation and growth of p-type μc-Si:H films using real-time SE. However, the differences between using the real-time SE and *ex-situ* SE to study μc-Si:H film have not been reported yet. This paper studied these differences. During the low temperature deposition of μc-Si:H films, there is a certain relation between the surface roughness and the growth mechanism. Toyama et al. [5] studied the surface roughness of boron-doped and undoped μc-Si:H films using AFM. The effects of boron doping on the surface roughness have not been studied using real-time monitoring methods. Real-time SE not only can obtain the surface roughness, but can also help analyze the growth mechanism.

In this paper, the differences between using real-time SE and *ex-situ* SE to study μc-Si:H film have been studied, and the effect of boron doping on surface roughness of μc-Si:H film using real-time SE was reported. Based on the KPZ model [19,20], the growth mechanism is discussed.

2. Experimental details

The μc-Si:H thin films were prepared in a cluster type radio frequency PECVD system. Silane (SiH_4), hydrogen (H_2) and borane (B_2H_6) were used as source gases. B_2H_6 was 30% diluted in hydrogen. The pressure was kept at 300 Pa. Two series of samples with intrinsic and boron doped thin films were prepared. The excitation frequency was 13.56 MHz. The substrate temperature was 150 °C, the electrode gap was 2.5 cm, and the background vacuum was kept at about 4×10^{-4} Pa. The input power was set at 150 W. The silane concentration was defined as $[SiH_4]/([H_2] + [SiH_4])$, and the value was 1%. Boron doped concentration was defined as $[B_2H_6]/[SiH_4]$, and the value was 0.5% with the total reaction gas flow of 200 sccm. The deposition time was varied from 10 min to 60 min. The glass substrate was washed by detergent, acetone, alcohol and deionized water, respectively, and then dried by nitrogen. The film thickness and surface roughness were measured with spectroscopic ellipsometer (VASE, J. A. Woollam Company). The incidence angle was fixed at 70°, with the spectral range of 200–1000 nm and 10 nm measuring step. The measured ellipsometry parameters ψ and Δ were analyzed using the WVASE32 software. The film crystallinity was characterized by Raman spectroscopy using a Renishaw 2000 Raman spectrometer with 632.8 nm laser excitation and 5.32 mW output power.

3. Results and discussion

Spectroscopic ellipsometry is a nondestructive method, which measures the state of polarization of the incident light and analyses the reflected light. The fundamental equation of ellipsometry is:

$$\rho = \frac{r_p}{r_s} = \tan \psi e^{i\Delta} \tag{1}$$

where ρ is the ratio of the complex Fresnel reflection coefficients. The ellipsometric parameters ψ and Δ can depict the change of polarization state of the light waves before and after reflection. The change of ψ and Δ is related to the films properties, thickness, surface roughness and so on [16]. The first crucial step of characterizing the film properties using SE is to choose the suitable model. The Bruggeman effective medium approximation (BEMA) model is an effective method to calculate the silicon films properties with a certain degree of crystallinity [21]. Hydrogenated microcrystalline silicon thin film is a complex phase material containing microcrystalline grains, grain boundaries, voids and amorphous silicon. It has been reported that its dielectric function can be depicted with the BEMA model [22]. For fitting the SE data, the μc-Si:H thin films can be regarded as a three-layer. For the μc-Si:H thin films, there is an amorphous incubation layer in the initial growth progress. The amorphous incubation layer has a great influence on the properties of the films. An amorphous incubation layer formed during the initial growth progress was added in the fitting model. In this study, three-layer fitting model was established so that it was more close to the actual conditions. Fig. 1 shows the three-layer model, which contains the incubation layer, bulk and surface roughness layers. The surface roughness layer consists of 50% silicon film and 50% of the cavities. The film total thickness is the sum of amorphous incubation layer thickness d_i and the bulk layer thickness d_b and 0.5 times surface roughness layer thickness d_s. It is assumed that both crystalline and amorphous phases are three dimensional objects. The thickness and volume ratio of each layer were fitted with linear regression, letting the δ^2 value reach the minimum. Here, δ^2 is a reference value used to identify a better fit [15].

$$\delta^2 = \frac{1}{N-m-1}\sum_{i=1}^{N}\left[\left(\tan\psi_{\exp} - \tan\psi_{calcu}\right)^2 + \left(\cos\Delta_{\exp} - \cos\Delta_{calcu}\right)^2\right] \tag{2}$$

Here, the subscripts "*exp*" and "*calcu*" express the experimental and calculated data, and N is the number of the experimental data points, while m is the number of fitting parameters. In this study, each layer thickness was obtained by ellipsonmetry data fitting. The influence of boron doping on the film growth was also analyzed by fitting the SE data.

The growth mechanism can be obtained by surface roughness inversion. According to the Kardar-Parisi-Zhang (KPZ) model [19], the relationship between the film surface roughness and thickness is $d_s \sim d^{\beta}$, where β is the growth index. Different β values correspond to different growth mechanisms [23]. $\beta = 1/2, 1/3$ and 0 denote the processes of zero diffusion limited random growth, finite diffusion growth and step flow growth, respectively. The surface roughness varies with the film thickness.

The Raman spectra were obtained to verify the feasibility of using elliptical polarization spectroscopy to characterize silicon thin films [24]. Fig. 2(a) shows the Raman spectroscopy data of microcrystalline silicon thin films with high X_c. Its X_c can be

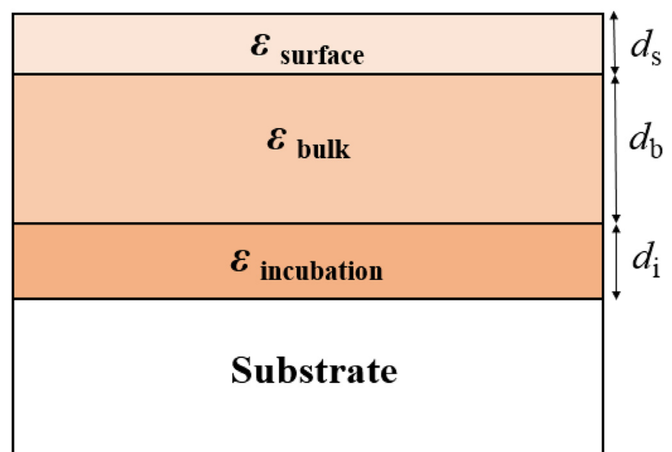

Fig. 1. The three-layer model for ellipsometry data fitting.

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